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PATENT APPLICATION
DEVICE BASED ON COATED NANOPOROUS STRUCTURE

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DEVICE BASED ON COATED NANOPOROUS STRUCTURE

FIELD OF THE INVENTION

This invention is directed to photovoltaic devices and more particularly to nanostructured photovoltaic devices and methods for manufacture of nanostructured photovoltaic devices.

BACKGROUND OF THE INVENTION

Many devices could benefit from an active layer having a network of regularly interconnected nanometer scale pores, including optoelectronic devices (e.g. photovoltaic cells, organic LEDs, and lasers), optical devices (e.g. waveguides and optical filters), mechanical devices (e.g. filters and separation media), and chemically-active devices (e.g. catalysts. In each of these and other device applications, it would be beneficial to have a nanometer-scale network comprised of either semiconducting (e.g. semiconducting metal oxides), conducting materials (e.g. metals), and/or sequentially placed conformal layers of semiconducting and conducting materials as a component of such devices.

Recently, mesoporous templates have been fabricated using sol gel surfactant templation techniques. Examples of such surfactant-templation techniques for producing porous films are described, e.g., by Brinker, et al in U.S. Patent 6,270,846, the disclosures of which are incorporated herein by reference. Such sol gel techniques can fabricate mesoporous metal oxide templates, which can be semiconducting. However, templates fabricated in this fashion often have an irregular pore structure with undulating channels as illustrated schematically in FIG. 1. The undulating channels make it difficult to incorporate material. Further, the types of metal oxides which can be formed using sol gel techniques are limited. In addition, conducting metal materials cannot be formed using sol gel techniques.

Sol gel techniques can fabricate silica templates with straight channels that intersect at right angles, as depicted schematically in FIG. 2. Unfortunately, silica is highly insulating and therefore not suitable as a semiconducting or conducting material. Furthermore, even the pore structure of FIG. 2 is difficult to fill or coat. Specifically, there is no satisfactory way to uniformly deposit material in both the horizontal pores as well as the vertical pores.

Thus, there is a need in the art, for a device containing regularly interconnected nanometer scale pores that are uniformly coated on their surface that overcomes the above difficulties and a corresponding method for making such a device.

BRIEF DESCRIPTION OF THE DRAWINGS

The teachings of the present invention can be readily understood by considering the following detailed description in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic three-dimensional diagram of a first porous nanostructure according to the prior art;

FIG. 2 is a schematic three-dimensional diagram of a first porous nanostructure according to the prior art;

FIG. 3 is a schematic three-dimensional diagram of a portion of a nanostructured active layer according an embodiment of the present invention; and

FIG. 4 is a vertical cross-sectional schematic diagram illustrating a photovoltaic device according to an embodiment of the present invention.

DESCRIPTION OF THE SPECIFIC EMBODIMENTS

Although the following detailed description contains many specific details for the purposes of illustration, anyone of ordinary skill in the art will appreciate that many variations and alterations to the following details are within the scope of the invention. Accordingly, the embodiments of the invention described below are set forth without any loss of generality to, and without imposing limitations upon, the claimed invention.

According to embodiments of the present invention, a device may include an active layer having a mesoporous template having an array of regularly spaced pores. An active material may be deposited on the walls of the pores in a way that conformally coats the walls to a substantially uniform thickness.

FIG. 3 depicts an example of a part of a nanostructured apparatus **300** according to an embodiment of the present invention. The apparatus **300** generally includes a mesoporous template **302** having a network of regularly spaced pores **304** (shown in phantom). One or more layers of materials **306**, **308** coat the interior walls of the pores **304** in a substantially conformal fashion. The nature of the materials **306**, **308** depends on the nature of the device in which the active layer **300** is used. For example, reactants and/or catalysts may participate in chemical reactions taking place within the pores **304**. Alternatively, the materials **306**, **308** may participate in physical reactions, such as light absorption, charge-splitting, light emission, charge transfer, charge storage, electrical or thermal conduction and the like, taking place within the pores **304**.

A characteristic dimension of the pores **304** (e.g., pore diameter or center-to-center pore spacing) is between about 1 nm and 50 nm. In a preferred embodiment, the pores **304** are substantially straight in at least one direction. By way of example, the pores **304** may include one or more sets of substantially straight pores. Each set of pores may be aligned parallel to one of three substantially perpendicular axes *x*, *y*, *z* and may intersect as shown in FIG. 3. By way of example, the template **302** may be made of silica (SiO_2), with a porous structure of the type depicted in FIG. 2. Alternatively, the template may be made of a conducting or semiconducting material and may have a pore structure of the type shown in FIG. 1.

A silica-based structure, such as that depicted in FIG. 3, could serve as a three-dimensional template to construct a component for a variety of devices. For example, if the walls of the pores **304** were coated with a semiconducting metal oxide, the apparatus **300** could be used as the active layer of an optoelectronic device such as a solar cell if the layer(s) of material(s) **306**, **308** include, e.g., a light-absorbing semiconducting material with differential electron affinity. In another example, materials **306**, **308** include a non-reactive metal such as gold or silver or other non-reactive material, the apparatus **300** may provide a robust mechanical filter comprised of an inert surface that could remove particles above the template pore size from a liquid or gas media, and where the mechanical strength imparted by the metal coating may increase the pressure of the carrier medium (liquid or gas) that can be passed through the filter. In addition to gold or silver, other non-reactive metals that could be coated onto the structure include the heavier elements of Group VIIB in the periodic table (sometimes called the platinum metals). In such a case, it is desirable that these or similar materials **306**, **308** do not completely fill up the pores **304**.

In a third example, the materials **306**, **308** may include a more reactive metal or other reactive material such as aluminum, magnesium, or calcium, such that the apparatus may act as a catalyst having a reactive surface that could increase the rate of a chemical reaction. In addition, such a structure could serve as both a filter and a catalyst. Furthermore, the materials **306**, **308** may exhibit specific optical properties including but not limited to particular optical transmission, reflection, absorption or other properties. Thus, the apparatus **300** may act as optical devices such as luminescent, electro-optic, and magneto-optic waveguides, optical filters, optical switches, amplifiers, laser diodes, multiplexers, optical couplers, and the like. Optical materials suitable for incorporation into optical devices include Nb-doped semiconductive SrTiO (NST), as well as $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}$ (PLZT), which has a higher electro-optic coefficient than LiNbO (Lithium Niobate), a widely used electro-

optic material. Other suitable materials include BaTiO. More generally, the range of thin films suitable for such devices includes ferroelectrics, dielectrics, and glasses, with epitaxial or glass structures. Many of these materials can be readily deposited from metal organic precursors that are chemically compatible with ALD processes.

- 5 In addition the apparatus 300 may be used in sensors, e.g. chemical and biological sensors, where the layers 306, 308 include a semiconducting or conducting surface coating that can transmit electrical signals arising from binding of a chemical or biological molecule to the very high surface area of the nanoscale network of the mesoporous template 302. Such coatings could serve to transmit electronic information, e.g., in the form of charge arising from a detection event. Examples of suitable coatings include, but are not limited to, coatings that are electrically conductive (e.g. metallic) coatings, such as Copper, Platinum, and Silver.

By way of example and without limitation, the mesoporous template 302 may be made from a precursor sol by surfactant templation as described, e.g., in US Patent 6,270,846. The precursor sol may include one or more covalent metal complexes with a central element X, one or more surfactants, one or more condensation inhibitors, water, and a solvent. Generally speaking, the molar ratios of the surfactant, condensation inhibitor, ethanol and water may be in the following ranges with respect to the central element X:

- [Surfactant]/[X]: a molar ratio ranging from about 1×10^{-7} to about 0.1
- 20 [Solvent]/[X]: a molar ratio ranging from about 3 to about 50
- [Condensation Inhibitor]/[X]: a molar ranging ratio from about 1×10^{-5} to about 5
- [water]/[X]: a molar ratio ranging from about 0 to about 20.

The central element X may be a metal, particularly a transition metal such as, e.g., Ag, Au, Cd, Co, Cr, Cu, Fe, Ir, Mn, Mo, Nb, Ni, Sr, Ta, Ti, V, W, Y, Zn, Zr, etc. Other suitable central elements X include Al, B, Ba, Ce, Ge, Hf, In, La, Pb, Os, Se, Si, Sn, Sr, or Va. The covalent metal complexes can be metal alkoxides and/or metal halides nitrides etc, including e.g., tetramethylorthosilicate, tetraethylorthosilicate, titanium butoxide, titanium isopropoxide, zirconium n-butoxide, aluminum isopropoxide, aluminum iso-propoxide and mixtures thereof. In a preferred embodiment the central element X is silicon (Si) and the mesoporous template is made of SiO₂ (silica) For SiO₂-based surfactant templated films examples of suitable alkoxides include polysiloxanes such as tetraethylorthosilicate (TEOS). For TiO₂-based porous surfactant templated films examples of suitable covalent metal

complexes include alkoxides such as titanium ethoxide or titanium isopropoxide, titanium chloride, titanium butoxide, titanium (AcAc) (i.e., titanium diisopropoxide(bis-2,4-pentanedionate)), titanium methacryloxyethylacetoacetate triisopropoxide, and titanium bis(triethanolamine) diisopropoxide and the like. The solvent can be a polar organic solvent or any other solvent that solubilizes the other reactants. Examples of suitable solvents include alcohols, (e.g., methanol, ethanol, propanol, butanol, isopropanol), tetrahydrofuran, formamide, dimethylformamide or mixtures thereof.

Examples of suitable surfactants include $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n(\text{CH}_2\text{CHCH}_3\text{O})_m(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, where the subscripts m and n are integers. A particular surfactant of this type is the block copolymer poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) (sometimes known commercially as Pluronic P123), for which $n=20$, $m=70$, $n=20$. Alternatively, a triblock copolymer (sometimes known commercially as Pluronic F127) for which $n=106$, $m=70$, $n=106$ may be used. Other suitable surfactants include hexadecyl trimethylammonium bromide (CTAB), polyoxyalkylene ether, and poly(oxyethylene) cetyl ether (e.g., Brij56 or Brij58). Pluronic is a registered trademark of BASF Corporation of Ludwigshafen, Germany. Brij is a registered trademark of Atlas Chemicals of Wilmington Delaware. Brij 56 is polyoxyethylene 10 cetyl ether. Brij 58 has several synonyms, including poly(oxyethylene) cetyl ether, poly(oxyethylene) palmityl ether, polyethylene oxide hexadecyl ether, and polyethylene glycol cetyl ether.

Examples of suitable condensation inhibitors include acids such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid (HNO_3), carboxylic acids, such as acetic acid (HOAc), and the like, bases such as sodium hydroxide (NaOH), ammonium hydroxide (NH_4OH) triethylamine, and the like, and chelating agents, such as ketones, B-diketones, carboxylic acids, B-keto-carboxylic acids, diols, aminoalcohols, crown ethers, hydroxyl or amine containing polymers, small molecules or cosolvents such as ethyl acetoacetate, 2-4-pentadione, acetone, diacetone alcohol, chatecol, stearic acid, lactic acid, chatechol, ethanolamine, triethanolamine and the like.

The sol may be filtered and a thin layer of the sol may be disposed on a substrate, e.g., by spin-coating, web-coating, dip-coating, spray-coating, ink-jet printing, doctor blade coating, spray coating, printing such as screen-printing, ink-jet printing, flexographic printing, gravure printing, micro-gravure printing, and the like. The solvent is evaporated from the sol to form a surfactant-templated film. Pore diameter and pore spacing in the surfactant templated film may be adjusted by (1) choice of surfactant, (2) concentration of surfactant, (3) the use of

block co-polymers, (4) temperature, (5) humidity level, (6) deposition procedure and speed, (7) concentration of covalent metal complex, (8) use of cosolvents, (9) swelling agents, (10) chelating agents, (11) acids, or (12) bases, (13) the nature of the covalent metal complex, e.g., in terms of type and nature of ligands attached, or some combination of two or more of (1)-
5 (13). Examples of these are described, e.g., in commonly assigned co-pending US Patent Application Serial Number 10/427,749, which is incorporated herein by reference.

The surfactant-templated film may be covalently crosslinked, e.g., by heating, to form the mesoporous template **302**. During this step, the surfactant templates can be also be selectively removed, e.g., through exposure to heat. For example, heating the as-coated film
10 to between about 170°C and about 400°C is typically sufficient to covalently crosslink the mesoporous template and/or decompose the surfactant molecules while remaining within the thermal stability range of the underlying substrate. Incubation temperature, ramp rate and total incubation time may be varied to optimize the properties of the film.

Although the mesoporous template is described as being fabricated by surfactant templation,
15 other techniques may be used. Examples of alternative techniques for forming the mesoporous template include, but are not limited to: (a) intercalation and/or grafting of organic or polymeric molecules within a mineral lamellar network; (b) synthesis by electrocrystallisation of hybrid molecular assemblies; (c) impregnation of preformed inorganic gels; (d) synthesis from heterofunctional metallic alkoxides metallic halides or
20 silsesquioxanes; (e) synthesis of hybrid networks through the connection of well-defined functional nanobuilding blocks; (f) templated growth of inorganic or hybrid networks by using organic molecules, macromolecules, proteins or fibers as structure directing agents; and (g) templated growth using nanoparticles as structuring agents followed by removal of the nanoparticles.

25 After the mesoporous template **302** has been formed the active material **306**, **308** may be deposited on the interior walls of the pores **304**. By way of example, the active materials may be deposited by atomic layer deposition. Atomic Layer Deposition (ALD) is a high-quality thin-film deposition technique based on sequential, self-limiting surface reactions. In
30 ALD a substrate is sequentially exposed to two or more reactant vapors while maintaining the substrate temperature within a temperature range favorable to the desired ALD reaction. A typical ALD process involves two sequential surface reactions involving two different reactants referred to herein as A and B. The ALD system may be purged of reactant gas between the A and B reactions with a non-reactive purge gas. The AB reaction sequence

forms a very thin layer of material, e.g., as little as one atomic layer, or a partial atomic monolayer, on the walls of the pores **304**.

Films deposited by ALD tend to be uniform over large areas. In addition ALD allows deposition of conformal films on structures having very high aspect ratios (e.g., > 100). So long as the spaces to be coated, e.g., gaps or pores, are larger than the ALD reactant gas molecules, the reactant gases can diffuse into the spaces. A wide variety of materials may be deposited by ALD, including semiconductors, metals, oxides, nitrides, and other materials. ALD techniques can thus deposit thin films one atomic layer at a time, in a "digital" fashion. The thickness of the ALD deposited film depends on the number of repetitions of the A/B deposition reaction sequence. Such "digital" build-up of material simplifies thickness control, thus reducing both complexity and cost. Another advantage of ALD is that it may be carried out at temperatures as low as room temperature.

By way of example, the layers of material **306**, **308** may include a layer of titania (TiO_2). Other suitable semiconducting materials include any of several metal oxides, e.g., zinc oxide, zirconium oxide, hafnium oxide, and the like. By way of example, where reactant A may be TiCl_4 and reactant B may be water vapor (H_2O), the two half-reactions may deposit a layer of TiO_2 . Atomic layer deposition using these reactants is described, e.g., by M. A. Cameron, et al., in "Atomic Layer Deposition of SiO_2 and TiO_2 in Alumina Tubular Membranes: Pore Reduction and Effect of Surface Species on Gas Transport," *Langmuir* **2000**, 16, 7425-7444, American Chemical Society, Washington D.C., which is incorporated herein by reference. In addition to oxides, layers of metals and other materials may also be deposited by ALD.

Additional layers of materials may be deposited on the walls of the pores **304** in subsequent processing steps (e.g., additional ALD or other deposition steps). It is also possible to completely or nearly completely fill the pores in the template **302** with additional material, e.g., by ALD, electrodeposition, electroless (chemical bath) deposition, or other techniques. By way of example, and without loss of generality, the pores **304** may be coated or filled with organic materials (e.g., a polymers, fullerenes, pigments, dyes, or small molecules) at room temperature by exposing the polymer to solvent vapor while on or mixed with the mesoporous template **302**. Solvent vapor infiltration techniques are described, e.g., in US Patent Application 10/719,041, which is incorporated herein by reference.

The nanostructured apparatus **300** may provide a three-dimensional layer having a network of regularly interconnected nanometer scale pores useful as a component for several different

types of devices including optoelectronic devices (e.g. photovoltaic cells, light emitting devices, e.g., organic light-emitting diodes (LEDs), and lasers), optical devices (e.g. luminescent, electro-optic, and magneto-optic waveguides, optical filters, optical switches, amplifiers, laser diodes, multiplexers, optical couplers, and the like), mechanical devices (e.g. filters and separation media), and chemically-active devices (e.g. catalysts).

By way of example, FIG. 4 depicts an optoelectronic device **400** having an active layer **401** with a mesoporous template **402** of the type described above may be disposed between first and second electrodes **403**, **405** (one of which may be transparent). For optoelectronic devices, it is often extremely desirable that the template **402** be made of an optically transparent or translucent material. Optional encapsulant layers **407**, **409**, e.g., glass or Mylar may protect the device **400**. A first semiconductor material **406** coats the interiors of pores in the template **402**, e.g., to a thickness of about 10 nm to about 30 nm. An (optional) second semiconducting material **408** may coat the first, e.g., if the template **402** is made of an insulating material, such as silica. In such a case, the first semiconductor material **406** may make electrical contact with the first electrode **403**. The nanostructuring of the template **402** provides a large area interface between the semiconductor materials **406**, **408** or between the first semiconductor material **406** and the template **402**.

The choice of semiconductor materials depends, in part, on the nature of the optoelectronic device. For example, the semiconductor materials **406**, **408** may be chosen so that the device **400** acts as a light-emitting device such as an LED or laser. For example, the device **400** may be configured as an LED if the materials **406**, **408** are doped such that they act as a PN junction that gives off light when biased in the forward direction. An LED-type device may be configured as a semiconductor laser, e.g., by suitable doping and/or reflecting surfaces configured to provide a resonant cavity for the emitted light to promote stimulated emission. Furthermore, the device **400** may be configured as a photovoltaic device if the materials **406**, **408** have complementary charge transfer properties with respect to each other (e.g., different affinity levels) and at least one of the two semiconductor materials **406**, **408** absorbs light.

By way of example, for photovoltaic devices and LEDs, the first and second semiconductor materials **406**, **408** may include inorganic materials, such as titania (titanium oxide, TiO_2), zinc oxide (ZnO), zirconium oxide, lanthanum oxide, niobium oxide, tungsten oxide, tin oxide, copper oxide, strontium oxide, calcium/titanium oxide, indium oxide, tungsten oxide, vanadium oxide, zirconium oxide, molybdenum oxide, vanadium oxide, strontium oxide, sodium titanate, potassium niobate, silicon (e.g., p-type or n-type doped), cadmium selenide

(CdSe), cadmium sulfide (CdS), cadmium telluride (CdTe), cadmium telluride selenide (CdTeSe), cadmium indium diselenide (CdInSe₂, CIS), cadmium indium Gallium diselenide (CdInGAsSe₂, CIGS) as well as blends or alloys of two or more such materials.

The second semiconductor material **408** may be inorganic or organic. Examples of suitable organic materials for photovoltaic devices include conjugated polymers such as poly(phenylene) and derivatives thereof, poly(phenylene vinylene) and derivatives thereof (e.g., poly(2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV), poly(para-phenylene vinylene) (PPV)), PPV copolymers, poly(thiophene) and derivatives thereof (e.g., poly(3-octylthiophene-2,5,-diyl), regioregular, poly(3-octylthiophene-2,5,-diyl) regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT), regiorandom, poly(3-hexylthiophene-2,5-diyl)), poly(thienylenevinylene) and derivatives thereof, and poly(isothianaphthene) and derivatives thereof. Other suitable polymers include organometallic polymers, polymers containing perylene units, poly(squaraines) and their derivatives, and discotic liquid crystals. Other suitable organic materials include organic pigments or dyes, azo-dyes having azo chromophores (-N=N-) linking aromatic groups, phthalocyanines including metal-free phthalocyanine; (HPc), Cu phthalocyanine (CuPc), Zinc phthalocyanine (ZnPc), perylenes, naphthalocyanines, squaraines, merocyanines and their respective derivatives, poly(silanes), poly(germinates), 2,9-Di(pent-3-yl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetrone, and 2,9-Bis-(1-hexyl-hept-1-yl)-anthra[2,1,9-def:6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetrone and small organic molecules such as pentacene and/or pentacene precursors. Blends of two or more of these materials can be combined as well.

In photovoltaic device embodiments where the template **402** is itself made from a semiconducting material, it is desirable for the template **402** and first semiconducting material **406** to have complementary charge transfer properties with respect to each other (e.g., titania and copper oxide). In other embodiments, it may be desirable to solution coat the template **402** (if semiconducting) or first semiconductor material **406** with an interfacial layer of, e.g., a ruthenium dye or functionalized fullerene (e.g., C₆₀). The use of interfacial layers in optoelectronic devices is described e.g., in commonly assigned U.S. Patent Application 10/419,708, which is incorporated herein by reference.

In some embodiments, it may be desirable to (optionally) coat or fill portions the template **402** with a conductive material **410**, which may be either organic or inorganic. The conductive material may cover a portion of a surface of the active layer to enhance electrical contact between one of the semiconductor materials (**406**, **408**) and one of the electrodes

(403, 405). By way of example, the conductive material 410 may be a transparent conductive polymer material (e.g., PEDOT, PEDOT or polyaniline doped with a dopant such as polystyrene sulfonic acid (PSS). Alternatively, the conductive material may be a transparent conductive oxide, e.g., indium tin oxide (ITO), fluorinated tin oxide (F:SnO₂) and the like.

- 5 Embodiments of the present invention provide for fabrication of a highly ordered three-dimensional mesoporous template that may be uniformly coated with a variety of different materials that cannot be otherwise self-assembled into such an ordered form. Consequently, highly efficient optoelectronic devices, e.g., light emitting devices (such as , organic LEDs, and lasers), photovoltaic devices (such as solar cells), optical devices (luminescent, electro-
10 optic, and magneto-optic waveguides, optical filters, optical switches, amplifiers, laser diodes, multiplexers, optical couplers, and the like), chemical devices (such as catalysts) and mechanical devices (such as filters for filtering gases or liquids) may be fabricated efficiently and economically.

- While the above is a complete description of the preferred embodiment of the present
15 invention, it is possible to use various alternatives, modifications and equivalents. Therefore, the scope of the present invention should be determined not with reference to the above description but should, instead, be determined with reference to the appended claims, along with their full scope of equivalents. The appended claims are not to be interpreted as including means-plus-function or step-plus function limitations, unless such a limitation is
20 explicitly recited in a given claim using the phrase "means for" or "step for."